

# FIRST YEAR PROGRESS REPORT

To

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NASA Kennedy Space Center

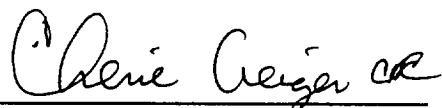
On

ENHANCEMENT OF IN-SITU ZERO-VALENT METAL  
TREATMENT OF CONTAMINATED GROUNDWATER

By


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## **SUMMARY**

Groundwater contamination by chlorinated solvents has been found at many sites. An innovative technique which has been the topic of numerous studies uses zero-valent metals to promote the reductive dehalogenation of chlorinated hydrocarbons. The purpose of this study was to evaluate the combined effects of sonication and zero-valent metal on the rate of destruction of chlorinated hydrocarbons. If degradation rates can be enhanced, reaction times will be reduced for equivalent final contaminant concentrations. Consequently, reactor size can be reduced in the application of this technology to field-scale projects, significantly decreasing treatment cost. Comparison of half-lives of trichloroethene when treated with iron suggests that the addition of ultrasound increases reaction rates more than three-fold over use of iron alone. Sand column studies have demonstrated that acid washed iron can completely degrade TCE to environmentally acceptable products. These studies have also shown that the iron loses activity as it ages. The application of ultrasound to the iron particles has been shown to reactivate the iron for the TCE degradation reaction.

### **1.0 TECHNICAL DISCUSSION**

#### **1.1 Background**

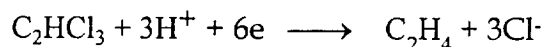
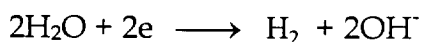
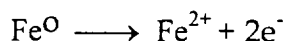
Chlorinated solvents are used by a wide range of industries including dry cleaners, electronic equipment manufacturers, metal parts fabricators, insecticide and herbicide producers, military equipment manufacturers, etc. These solvents replaced petroleum derived mineral spirits and have distinct advantages because of their nonflammability. The persistence and mobility of these hydrocarbons in the subsurface was largely unanticipated, therefore historical disposal practices have lead to widespread groundwater contamination. For example, trichloroethene (TCE) has been found at more than 791 of 1300 National Priority List sites (Clement International Corporation, 1993), primarily as a groundwater contaminant.

Treatment of chlorinated hydrocarbon contaminated groundwater is usually accomplished by pumping the groundwater to the surface and removing the contaminant through oxidation or air stripping. More recently, efforts have focussed on the physical, biological, or chemical treatment of these contaminants in place. An innovative technique which has been the topic of numerous laboratory studies, and more recently, several pilot and full-scale efforts, uses zero-valent metals to promote the reductive dehalogenation of chlorinated hydrocarbons (Gillham and Burris, 1992; and EPA, 1990). Abiotic reductive dechlorination has been facilitated by iron, cobalt, and nickel porphyrins and corrins, indicating the potential importance of metals and coenzymes to this reaction (Assaf-Anid et al, 1994).

Zero-valent zinc and iron significantly enhanced the reductive dehalogenation of aliphatic compounds with iron being particularly attractive due to its low cost and availability (Gillham, et al, 1993). Batch tests in which aqueous solutions of a wide range of chlorinated methanes, ethanes, and ethenes were added to 100-mesh iron filings resulted in degradation rates that were three to seven orders of magnitude greater than natural abiotic rates reported in the literature (Gillham and Burris, 1992). Generally, the rates increased with the degree of chlorination and

with increasing iron surface area to solution ratio. The chlorinated products of degradation subsequently degraded to non-chlorinated compounds. Similar results have been obtained by Vogan et al. (1994) who propose that the corrosion of iron, while occurring independently of volatile organic compound degradation, likely provides the electron source needed for the reduction.

Although the reaction mechanism for zero-valent metal catalyzed chlorinated solvent destruction is not precisely known, it appears to involve the simultaneous oxidation of iron by water and reductive dechlorination, as shown below for trichloroethene (TCE) (Matheson and Tratnyek, 1994):



Thus, the destruction of one mole of TCE yields three moles of chloride and results in a pH increase due to the consumption of protons. Degradation rates, however, have been found to decline with increasing pH (Gillham, et al, 1993) presumably because of surface deposition of iron precipitates. Laboratory studies generally account for most of the chloride mass generated (98 to 100 percent), however, carbon mass balances are usually much lower, probably due to the volatility of the carbon end products (Orth and Gillham, 1996).

The reductive dechlorination of chlorinated compounds has also been shown to be effectively accomplished using ultrasound (Bhatnagar and Cheung, 1994; Kotronarou, et al, 1992; Orzechowska, et al, 1995) with 100 percent destruction occurring within one hour (Bhatnagar and Cheung, 1994) suggesting that ultrasound could be a potent remedial technique for contaminated groundwater. Chlorinated byproducts were not detected.

The term ultrasonics is applied to periodic stress waves, often loosely referred to as either sound or acoustical waves, that occur at frequencies above the limit of human hearing, or in excess of 20,000 Hertz (cycles per second). Stress waves are aptly named because they create a deformation stress of the medium through which they are passing. At their upper extreme, ultrasonic frequencies are so high that their extremely short wavelengths are comparable to the agitation of molecules caused by heat (Heuter and Bolt, 1955).

The effects produced by high-energy ultrasonic waves are normally irreversible and arise from intense mechanical stresses and localized heating phenomenon known as cavitation. Cavitation occurs in those regions of a liquid which are subjected to rapidly alternating pressures of high amplitude. Although the presence of bubbles facilitates its onset, cavitation can also occur in gas-free liquids when the acoustic pressure amplitude exceeds the hydrostatic pressure in the liquid. For part of the negative half of the pressure cycle the liquid is in a state of tension. Where this occurs, the forces of cohesion between neighboring molecules are opposed and voids

are formed at weak points in the structure of the liquid. These voids grow in size and then collapse rapidly in the same way as gas-filled bubbles. At the end of the collapse, the gas within the cavity will be highly compressed, perhaps to hundreds of atmospheres. These high pressures will be relieved by the radiation of shock waves. The intense shock waves can cause liquids to mix that do not normally do so (such as oil and water); break up giant molecules such as polymers, proteins, and viruses; and initiate chemical reactions (Brown and Goodman, 1965).

Sonication has been applied to the destruction of compounds such as parathion (Kotronarou, et al, 1992), pentachlorophenolate (Petrier, et al, 1992), and chlorinated hydrocarbons (Cheung, et al, 1991). The mechanism for destruction has been hypothesized to involve the thermal dissociation of water during bubble collapse to produce hydroxyl radicals which react with target compounds (Bhatnagar and Cheung, 1994). In addition, thermal destruction (or pyrolysis) has been reported to occur within the cavitation bubble at the extremely high temperatures induced by sonication (Kotronarou, et al, 1992). The destruction of chlorinated hydrocarbons by sonication usually results in a decline in pH due to the production of hydrochloric acid. As is observed during zero-valent metal reactions, the rate of reaction increases with decreasing pH.

The purpose of the study described herein was to evaluate the combined effects of sonication and zero-valent metal on the rate of destruction of chlorinated hydrocarbons. Suslick and Casadonle (1987) observed that nickel particles were several hundred-fold more active in hydrogenation reactions after being sonicated. If degradation rates can be enhanced, reaction times will be reduced for equivalent final contaminant concentrations. Consequently, reactor or permeable wall size can be reduced in the application of this technology to field-scale projects, significantly decreasing treatment cost. The effects of ultrasound were examined using batch tests conducted in a laboratory reactor.

## **1.2 Project Objectives**

The objectives of this project are threefold: the first is to examine methods for using zero-valent metals in a permeable reactive wall to catalyze dehalogenation reactions at a rate that is practical and cost effective in groundwater remediation applications. The second objective is to develop a methodology for stabilizing and/or enhancing the rate of the dehalogenation reaction in the reactive wall over extended periods of time. The third objective is to examine new and more cost-effective techniques for building chemically reactive permeable treatment walls.

If these three objectives are met then it will be possible to design a permeable treatment wall that would be capable of containing and remediating sites contaminated with a chlorinated solvent. There is a tremendous need for such a technology, for present methodologies are typically not successful or cost-effective.

A summary of the individual steps in the work plan that will lead to meeting the objectives of this project are listed below:

1. Evaluate site specific problems at KSC where the permeable reactive wall technique would be applicable. Tailor subsequent tasks to recognize KSC specific issues.
2. Build laboratory-scale permeable reactive wall test assemblies using column technology.
3. Construct reactive walls in columns using the excavation and back-fill technique.
4. Investigate the rate of degradation of TCE and PCE through a reactive wall by using small zero-valent particles of iron and magnesium.
5. Investigate the control of pH and thereby the degradation rate in the reactive wall by using controlled release acids and buffers.
6. Investigate the reduction in pH and its effect on the degradation rate by using in situ injection of control solutions into the reactive wall.
7. Investigate the use of ultrasound to in situ activate a zero-valent loaded reactive wall.
8. Using an optimum reactive wall composition as determined from the data generated from the walls created by the backfill techniques, create reactive walls in the sand columns by using slurry techniques. Measure the rate of degradation of the slurry prepared reactive walls and compare to the backfill wall rates.
9. Build a laboratory scale aquifer simulation model.
10. Introduce an optimum composition reactive wall into the aquifer simulation equipment by the best technique established in this study.
11. Measure TCE and PCE dehalogenation rates and stability of the reactive wall in the aquifer simulator and compare to the sand column data.
12. Formulate a design for the construction and composition of a chemically active permeable reactive wall that could be used in a field test to remediate a groundwater contaminated with TCE or PCE or mixtures of both.

The work described in the steps outlined above is being conducted in the laboratories of the principal investigators which are located in the Department of Chemistry and the Department of Civil and Environmental Engineering.

## 2.0 EXPERIMENTAL RESULTS

### 2.1 Quality Assurance/Quality Control Plan

The initial phase of this project was concerned with establishing analytical procedures and a quality control plan. A copy of the QA/QC plan was submitted in the January, 1996 progress report on this project. This plan is currently being used to collect and analyze samples that are applicable to this project.

### 2.2 Batch Studies

Initial experiments concerned with studying the degradation of TCE by zero-valent metals were performed in a batch reactor. The purpose of these studies was to measure rate constants of various grades of iron and to observe the effect of ultrasound on their reactivation of dehalogenation.

#### 2.2.1 Methods and Materials

Batch Reactor. Aqueous samples of TCE were exposed to 20-kHz ultrasound in a 1-L batch reactor (three-neck round-bottom flask) shown schematically in Figure 1. Teflon wrapped glass stoppers were used at each neck to maintain gas-tight conditions. The reactor was filled with deionized water (1000 mL), a magnetic stirring bar, and 1 g of iron, and then purged with nitrogen gas. A TCE stock solution was prepared by dissolving one mL of TCE in ten ml of methanol. This stock solution was added to the batch reactor to give a final concentration of approximately five to 20 ppm. The reactor was maintained at a constant temperature of 25°C by submerging it in a water bath.

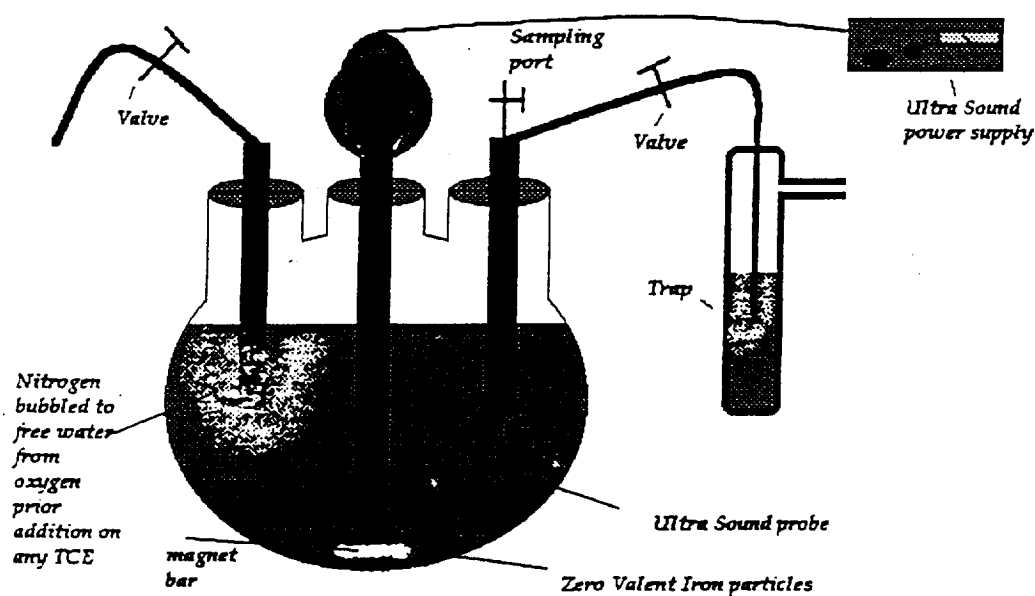


Figure 1. Schematic Diagram of Batch Reactor.

Ultrasound, when used, was introduced using a Fisher Sonic Dismembrator Model 300 ultrasonicator to produce 20-kHz frequency and deliver 300 W of power at maximum setting. Ultrasound was introduced at either 30 or 60 percent of maximum power. The 12-cm ultrasound probe (five mm indiameter) was submerged seven cm below the water surface. Sonication was continuous during each run.

Duplicate samples were removed from the reaction vessel using a 30-cm stainless steel needle and gas-lock syringe introduced through a septum at one of the three reactor necks. Simultaneously, nitrogen gas was introduced to displace the sample volume. Samples were placed in 11.4-ml screw-top, zero-head vials with Teflon-lined septa. The samples were immediately refrigerated at 4°C until analyzed. Tests showed that TCE loss through volatilization was negligible. Temperature was monitored continuously and pH was measured at the beginning and end of each run.

Materials. Reagents were obtained from Fisher Scientific, all at least 99 percent purity and used as recieved. One hundred-mesh iron, obtained from Mallinckrodt Chemicals (Paris, KY 40361) was used for most of the batch sutdies. However, other grades and sizes of iron were also tested.

Analysis. TCE was analyzed following EPA Method 624. Each sample was injected with 5.0 µL of internal standard, 5,000 ppm bromochloromethane in mehtanol. A five-ml portion of the sample was transferred to a purge vial. Helium was bubbled through the sample for a period of eleven minutes to transfer the TCE onto a Vocarb 3000 trap. The desorb time from the trap was four minutes at 250°C and the trap bake time was seven minutes at 260°C. A Hewlett-Packard gas chromatograph (Model 5890) equipped with a 0.25-mm id, 60-m long Vocol capillary column was programmed for a three-minute hold at 60°C, and a 15°C/min rise to 180°C held for three minutes.

Iron surface area was measured by using a Porous Material, Inc. BET Sorptometer and pH was measured using a Cole-Parmer Chemcadet 5986-25 pH/mV meter and probe.

### **2.2.2 Results**

Initial experiments were dedicated to the observation of TCE destruction in mixtures with increasing loading of iron powder. It was observed that destruction increased with increasing mass of iron. This is likely due to increased surface area available for iron/TCE contact and thus verifies the hypothesis that this is a surface area phenomenon. Figure 2. shows first order plots of data from three experiments using 1.0, 3.0, and 5.0 g Fe powder per liter of solution.



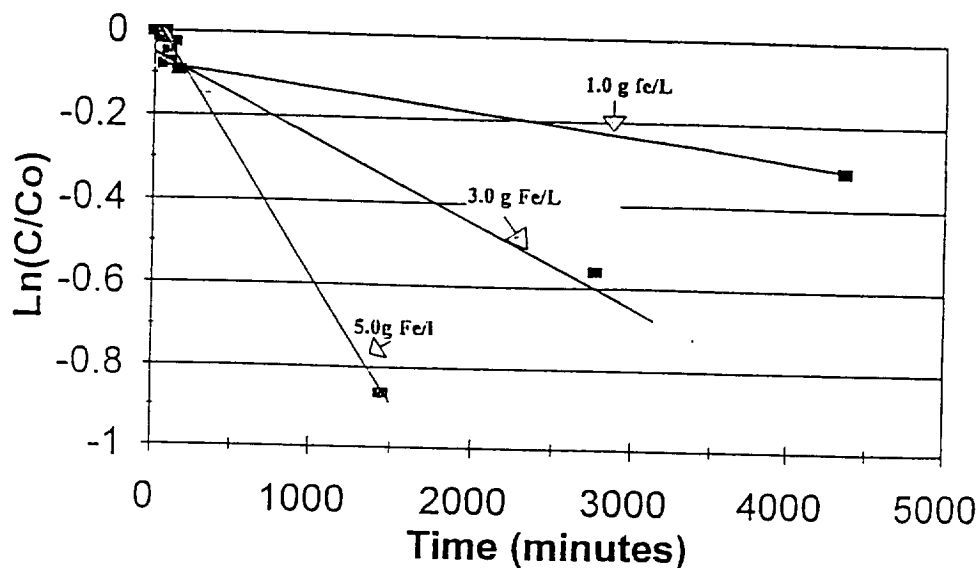


Figure 2. The effects of increasing amounts of Fe on the rate TCE destruction.

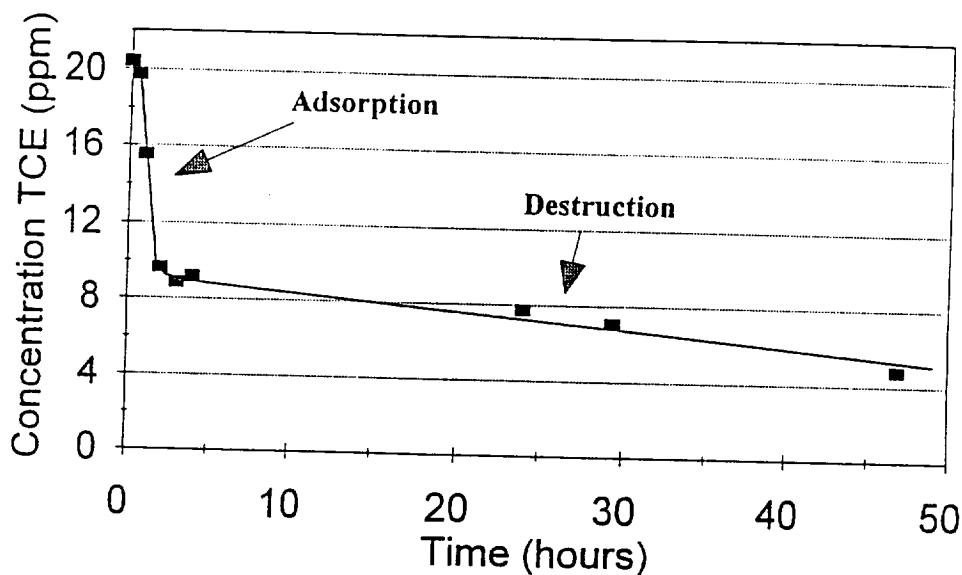


Figure 3. TCE removal by adsorption and destruction.

Samples taken during the first 120 minutes of the experiments provided data that did not correlate well with samples taken later in the experiments. When data from the entire experiment was plotted as a first order function, it became obvious that something different was occurring during the first two hours after the addition of iron. Early data did not fit a first order plot (correlation coefficients of 0.50 and lower) but later data fit a first order function with correlation coefficients of greater than 0.90. Figure 3. shows the fast drop in concentration during the first two hours and the constant rate of TCE disappearance (linear when plotted as a first order function,  $r^2=0.986$ ) that followed. A plausible explanation for this behavior is adsorption of TCE onto the iron surface.

In order to examine the effects of ultrasound on dechlorination of TCE, a series of experiments were run using the batch reactor shown in Figure 1. To determine possible TCE loss in the absence of iron and ultrasound, TCE was placed in the reactor and the concentration was monitored over a 20 hour period. Three grams of 100 mesh iron were then added and TCE concentration was monitored over an additional 48 hrs. As seen in Figure 4, TCE loss prior to the addition of iron was negligible while significant losses were observed in the presence of iron.

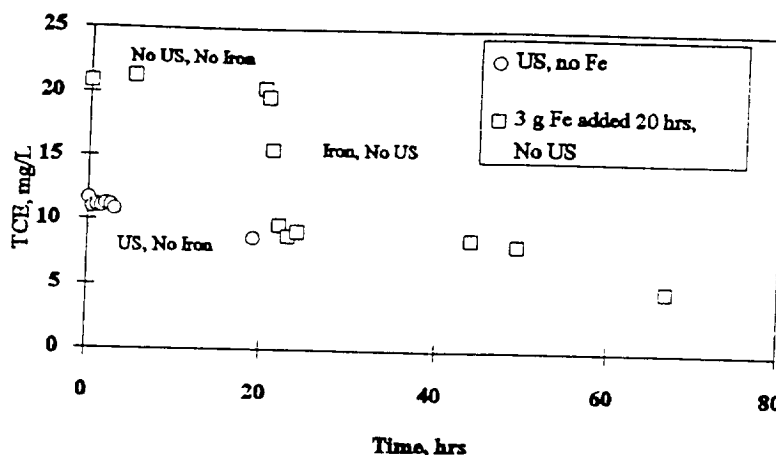


Figure 4. TCE Removal Using Zero-Valent Iron and Ultrasound

The collective impact of iron and ultrasound on TCE removal was evaluated using two parallel experiments. In one reactor, one gram of iron was initially added with ultrasound immediately introduced and continued over the next 48 hrs. After 48 hrs, ultrasound addition was discontinued and TCE concentration monitored for an additional 100 hrs. In a second reactor, the opposite pattern of ultrasound addition was practiced. One gram of iron only was utilized over the first 48 hrs. At 48 hrs, sonication was commenced and monitoring was continued for an additional 100 hrs. The results of these experiments are shown in Figure 5. In Figure 5 it can be seen that TCE removal is significantly more rapid where ultrasound is utilized, both initially and after 48 hrs.

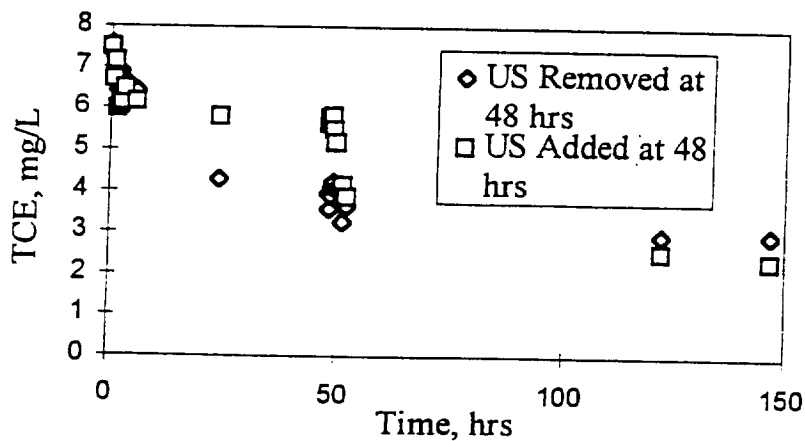


Figure 5. The Effect of Ultrasound on TCE Removal Using 1 g Iron

To quantify the results, data were analyzed assuming first order kinetics. Concentrations were transformed to natural logarithms and results of linear regression between transformed concentrations and time were examined. First order kinetic constants and half-lives are provided in Table 1. To permit comparison with results of other researchers, the half-lives were normalized to 1 m<sup>2</sup> of specific iron surface area per mL of solution volume. Normalized half-lives are similar to those found by other researchers, although the low surface area to solution volume ratio used in other studies ( $1.76 \times 10^{-3}$  to  $5.28 \times 10^{-3}$  m<sup>2</sup>/mL) has been found in other studies to yield disproportionately high half-lives (Gillham and O'Hannesin, 1994).

Table 1. Results of Batch Tests Using Iron and Ultrasound

<u>Conditions</u>	<u>g Iron</u>	<u>k, hr<sup>-1</sup></u>	<u>Half-life, hr</u>	<u>Half-life, hr*</u>	<u>pH initial/ pH final</u>
US	0	0.0147	47	--	7.6/7.8
US	1	0.0110	62	0.11	7.0/7.8
No US	1	0.0034	203	0.36	7.0/8.1
US	3	0.0426	16	0.084	--
No US	3	0.0218	32	0.17	--

**\*per m<sup>2</sup> of iron surface area**

The enhancement effect on the reaction rate of the ultrasound in the system also appears to be a function of the amount of iron particulate in the system. The ratio of rate constants for experiments comparing the use of ultrasound and iron with those using only iron declines as the iron loading increases. In experiments using only 1.0 g Fe/1.0L solution, the ratio of US/no US rate constants is 3.28. In experiments using 5.0 g Fe/1.0 L solution, this ratio drops to 1.42. This indicates that ultrasound, by itself, is not as effective for use in dehalogenation when particulate levels increase.

However, the opposite trend is observed when considering the effects of ultrasound on the iron particles. Parallel experiments were conducted to observe the effectiveness of iron powder that had never been exposed to ultrasound compared with iron that had previously been treated with ultrasound. Table 2. shows that in experiments with 1.0 g Fe, the effects of ultrasound exposure were not obvious. As iron loading was increased in further experiments, rate constant ratios increased to 1.92 for 3.0 g Fe and 5.00 for 5.0 g Fe.

Ultrasound has been used for several years to clean various materials including metal surfaces. The cleaning effects of ultrasound are more pronounced in these experiments at higher iron loading. Higher iron loading results in a more effectively cleaned surface area being exposed to catalyze the dehalogenation reactions.

Table 2. Rate Constants for Experiments With Ultrasound Treated and Untreated Iron

Rate Constants k (min <sup>-1</sup> )			
Fe(g)	No US Treatment	US Treated	Ratio
1	4.0 x 10 <sup>-5</sup>	4.0 x 10 <sup>-5</sup>	1.00
3	1.3 x 10 <sup>-4</sup>	2.5 x 10 <sup>-4</sup>	1.92
5	1.3 x 10 <sup>-4</sup>	6.5 x 10 <sup>-4</sup>	5.00

It is the nature of reductive dehalogenation that one species loses electrons and is “corroded.” In this reaction, the iron is expected to corrode, lose surface area and therefore some activity with time. Because ultrasound pre-treatment enhanced the degradation rates of TCE, further experiments were conducted using scanning electron microscopy (SEM) to verify that ultrasound could in fact remove the solids that form on the iron surface.

Iron was aged for one month in 200 ppm TCE solution, then removed and dried under nitrogen gas. Two equal portions of the iron were introduced into 10.0 ppm TCE solutions. Ultrasound was added to one reaction flask for 180 minutes, the solution was removed and the iron dried under nitrogen. The second flask received the same treatment but without ultrasound.

Samples from the aged iron, the portion exposed to ultrasound, and a portion from the second flask with no ultrasound treatment were examined using SEM. The aged iron showed significant corrosion with most of the surface area affected. The second flask that was not exposed to ultrasound had a similar appearance. However, the iron exposed to ultrasound for only 180 minutes was significantly cleaner. The areas of corrosion had decreased in size and coverage as compared to the iron that was not exposed. Because the reaction mechanism is assumed to be surface area dependent, an increase in surface area after ultrasound treatment should be of great importance for extending the useful life of an in-situ treatment.

## 2.3 Column Studies

For the purpose of studying the kinetics of the dehalogenation reaction under continuous flow conditions and to study the aging characteristics of a reactive wall, six treatment columns have been built and are being used in this study. Data collected from these columns will be used in the design of the field-scale treatment wall that will be built at KSC. In addition, these columns will be used to help optimize the use of ultrasound to regenerate aged reactive walls.

### 2.3.1 Methods and Materials

A schematic of the test columns that were used in this study is shown in Figure 6. Five columns were constructed from 9.42-cm diameter Lucite pipe that was 96-cm long. Each column was fitted with eight sample ports located 10-cm apart. Four of the columns were loaded with different types of iron. The types of iron that were used are: 50-mesh iron particles, acid-washed Peerless iron, unwashed Peerless iron, and acid-washed Master Builders iron. Each of these columns contained 20% by weight iron and 80% by weight construction grade sand. The

fifth column that served as a blank or control contained 100% sand. A sixth column that was used to identify intermediate degradation products was 5-cm in diameter and was two meters long.

Each column is fitted with sample ports that are located at 10-cm intervals along the length of the column. Some of the columns were equipped with an ultrasound probe while others had the capability of adding the probe. Flow to the column was provided by means of a high performance liquid chromatography pump that is controlled by a microprocessor and has a range of 0.10-mL/min to 80.0 mL/min. Studies thus far have primarily focused on flow rates of 0.8mL/min.

The test water sample is prepared by filling a 100-L Teflon-lined plastic bag with deoxygenated water. The water is then spiked with the desired amount of TCE. The test water is kept in the dark while a continuous sample is pumped from it into the column. Test samples are taken from the column by successively unplugging each test sample port and allowing the sample to flow into a 11.4 mL vial through a vented septum until the vial is full. This procedure is begun at the top of the column and continued to each lower sample port until samples have been extracted from all test ports, plus untreated feed from the test water bag and a sample from the exit of the treatment column. The samples are then analyzed by the same purge and trap GC procedure that was used for the analysis of the batch samples.

### **2.3.2 Results**

The 100% sand column was used to measure the effect that sand had on TCE destruction. Data from a typical analysis of samples taken from the sand column after more than 50 pore volumes of TCE spiked water had passed through the column are shown in Figure 7. As can be seen from the data, sand has no effect on the TCE concentration. Thus any change in TCE concentration in the iron-sand mixture columns can be attributed to the effect of the iron.

Typical data that has been collected from some of the test columns are shown in Figures 8 - 10. The porosity of the 50-mesh iron column is 0.40, and for the Peerless iron column it is 0.30. By using these porosities, column dimensions and water flow-rates, the residence times and pore columns were calculated.

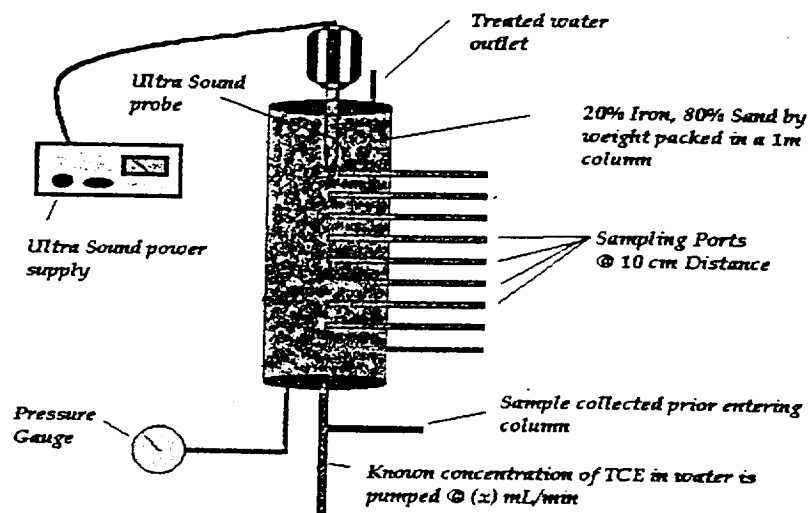


Figure 6. Schematic of test column.

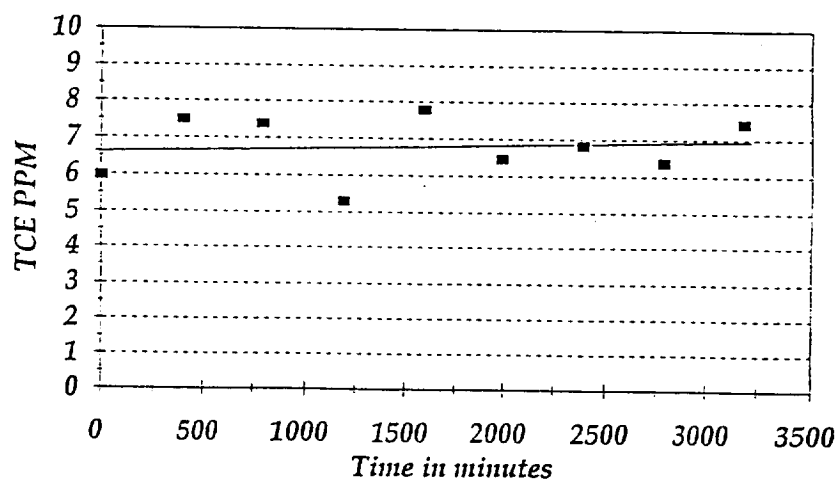


Figure 7. Plot of a TCE versus residence time in a 100% sand column at a flow rate of 0.8 mL/min.

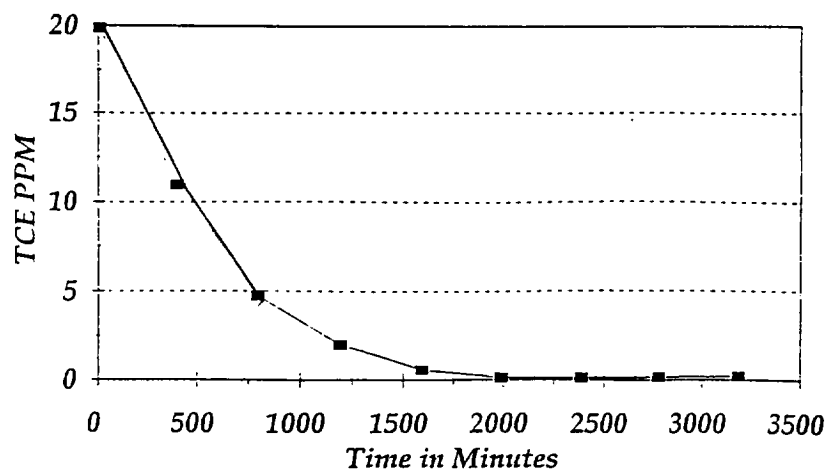


Figure 8. TCE destruction data for the 50-mesh iron/sand column at a flow of 0.8mL/min after 200 pore volumes.

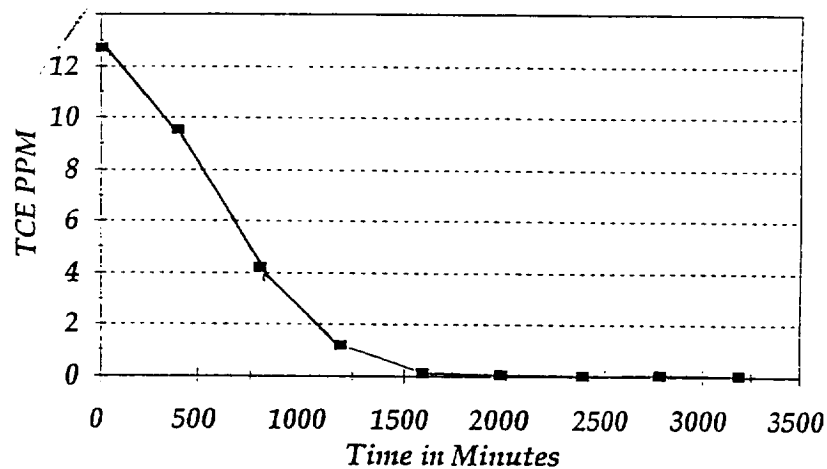


Figure 9. TCE destruction data for acid washed Peerless iron/sand mixture at a flow rate of 0.8mL/min after 50 pore volumes.

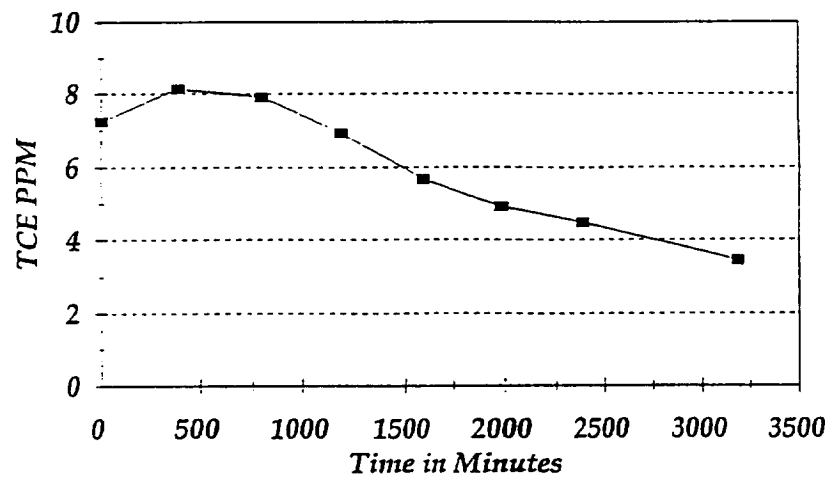


Figure 10. TCE destruction data for an unwashed Peerless iron/sand mixture at a flow rate of 0.8mL/min after 50 pore volumes.

The data in Figures 8 and 9 show that the TCE is totally degraded in the 50-mesh and acid washed Peerless columns, while in the unwashed Peerless iron column the TCE was not completely degraded before the water exited from the column.

For the purpose of calculating rate constants and half-lives, the data were fitted to a first-order kinetics rate equation. Typical plots are shown in Figures 11-13. The plot in Figure 11 is from the data shown in Figure 8, and those in Figures 12 and 13 are respectfully from the data shown in Figures 9 and 10. The statistical fit of this data shows excellent agreement with first order kinetics. A summary of the half-lives for the different columns is given in Table 3.

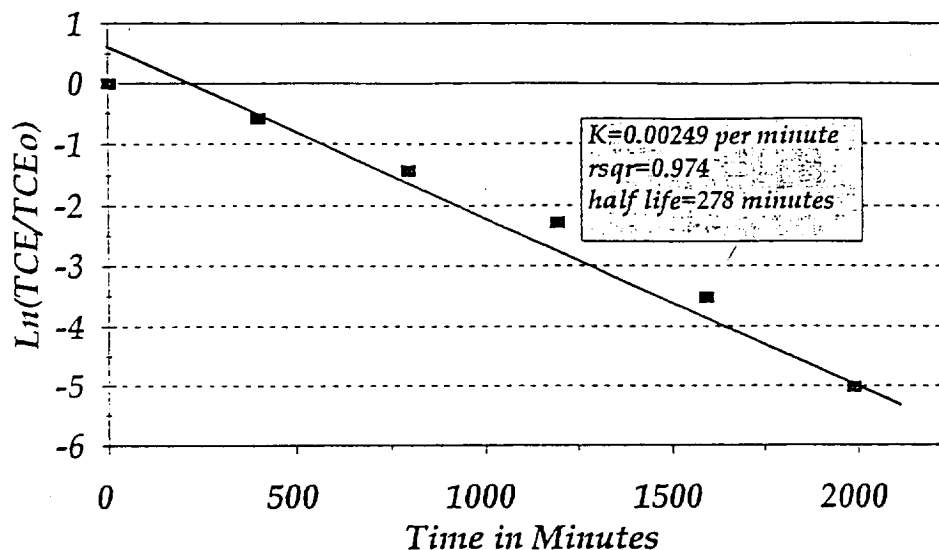


Figure 11. First order plot for TCE degradation in a 50-mesh iron/sand column after 200 pore volumes.

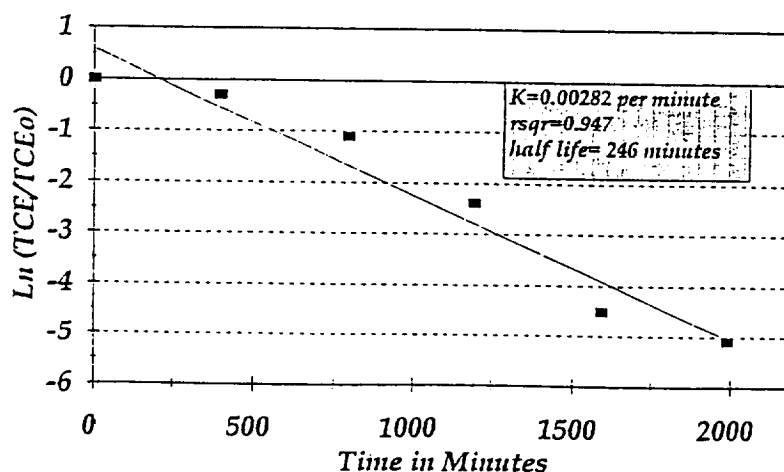


Figure 12. First order plot for TCE degradation in an acid-washed Peerless iron/sand column after 50 pore volumes.



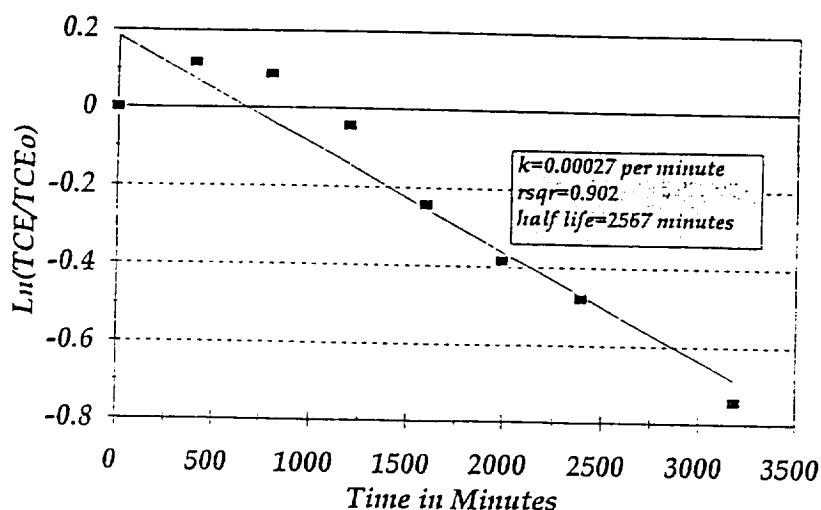


Figure 13. First order plot for TCE degradation in an unwashed Peerless iron/sand column after 50 pore volumes.

Analysis of the data in Table 3 leads to several observations. The first is that acid washing of the iron has a significant beneficial effect on the reactivity of the iron with regard to TCE degradation. For example, the acid-washed Peerless iron is ten times more reactive than the unwashed Peerless iron. The second observation is that there is not much difference in the half-lives of the three different types of acid washed iron that were tested. The third observation is that as the column ages with passage of water through it, the reactivity of the column decreases as shown by the increase in half-life of the 50-mesh iron from 240 minutes to 289 minutes after 225 pore volumes of water have passed.

TCE spiked water is continuously being passed through the columns and kinetic data is being collected. After the half-lives have increased to approximately twice their initial values, the columns will be treated with ultrasound to study the efficiency of reactivation by this technique.

Column	TCE Half-Life, min	No. of Pore Volumes
50 Mesh Iron	240	1-20
	289	200-225
Peerless Iron	246	50 - 60
Masterbuilder Iron	225	50 - 60
Unwashed Peerless	2567	50 - 60

Table 3. Half-Life Results for the Destruction of TCE in Reactive Iron Columns

## 2.4 Sandbox Studies

The technique that has been used thus far in the construction of reactive permeable walls has been to drive sheet pilings to create a box from which the soil is excavated and the box refilled with the reactive wall material. The sheet pilings are removed and the groundwater allowed to flow through the wall. The problem with this technique is that it is expensive and is limited to shallow depths. One of the objectives of this project is to investigate a new technique for building reactive walls. This technique consists of creating a series of boreholes which contain the reactive wall material. Because the porosity of the boreholes is greater than the surrounding soil, groundwater flow through the boreholes is facilitated. The boreholes are positioned in a geometrical pattern within a field so as to force all of the contaminated groundwater plume to flow through some part of the treatment wall. A schematic representation of a laboratory scale version of this borehole treatment wall is shown in Figure 14.

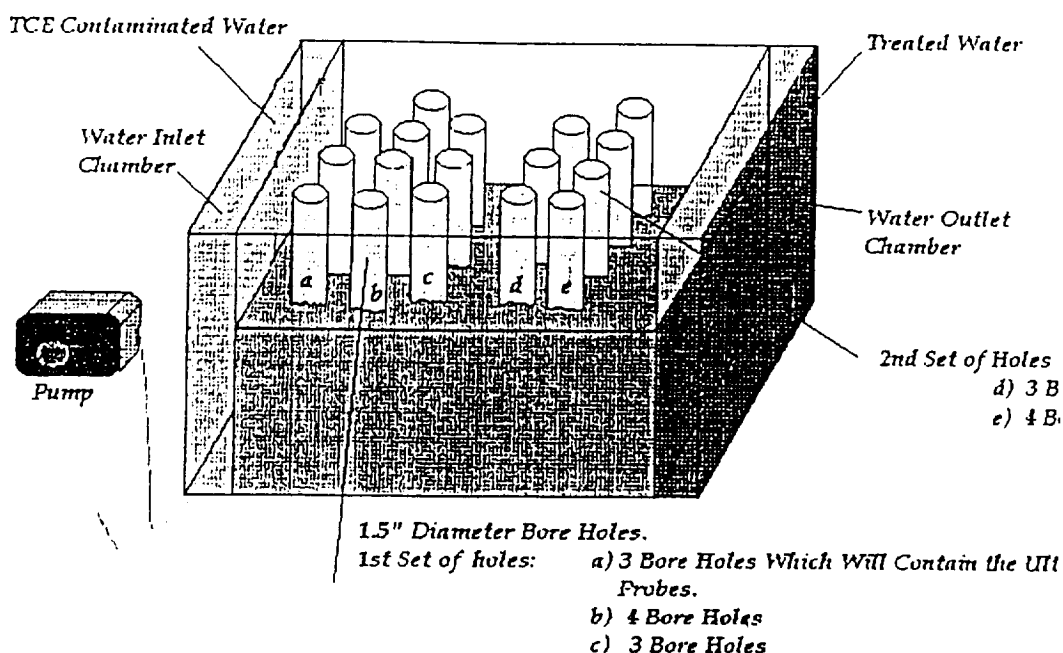


Figure 14. Schematic representation of a laboratory scale, "sandbox," reactive wall created by the borehole technique.

The illustration of the "sandbox" shown in Figure 14 represents a cut-away view of the borehole wall during its construction. The sandbox that has been constructed is a 1:20 scale version of the wall that will be built at KSC. The filled portion of the box is 50.8 cm high by 57.15 cm wide by 96.5 cm in length. The field contains 17 boreholes that are 4.7625 cm in diameter. The volume of the borehole material is 15.38 L. If this material was used to construct a continuous wall across the width of the box, the reactive wall would be 5.30 cm thick.

The front three boreholes will be treated with ultrasound by using three different probe techniques. One borehole will contain a permanent telescoping type of probe. The second borehole will contain a permanent spiral (e.g. auger design) type probe and the third borehole will be treated by augering in the spiral probe at the time of treatment. The different methods for

applying ultrasound treatment to regenerate the reactivity of the boreholes will be evaluated and the most efficient and economical method adopted for use in the field-scale tests at KSC.

### 3.0 CONCLUSIONS

Studies that have been conducted during this project have demonstrated that TCE in groundwater can be completely degraded to environmentally safe by-products by passage through a reactive wall containing elemental iron. In order to achieve high TCE degradation rates in the wall, it has been established that the iron surface must be cleaned by the use of an acid wash. TCE degradation rates for new walls using acid washed iron have been in the order of magnitude of 250 minutes for the half-life. As the iron in the wall ages, the rate of TCE degradation has been found to decrease. This decrease in rate has been found to be due to surface contamination of the iron with products formed from the TCE degradation reactions. It has been demonstrated that the effect of the by-products on the reactivity of the iron can be minimized by the application of ultrasound to the reactive wall. Studies are continuing on this project with the objective being the development of materials and a methodology for creating and maintaining a reactive groundwater treatment wall through feasible economical engineering processes.

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